

(19)  Canadian
Intellectual Property
Office

An Agency of
Industry Canada

Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

(11) **CA 2 352 182** (13) **A1**

(40) 08.06.2000
(43) 08.06.2000

(12)

(21) 2 352 182

(51) Int. Cl. 7: **A22C 13/00**

(22) 17.11.1999

(85) 24.05.2001

(86) PCT/EP99/08824

(87) WO00/32050

(30) 198 54 769.2 DE 27.11.1998

(71) WOLFF WALSRÖDE AG,
D 29655, WALSRÖDE, XX (DE).

(72) KRALLMANN, ANTON (DE).
POPHUSEN, DIRK (DE).

(74) FETHERSTONHAUGH & CO.

(54) BOYAU EN MATIÈRE PLASTIQUE PERFORÉ PAR LASER
(54) PLASTIC GUT PERFORATED BY A LASER

(57)

The present invention relates to a biaxially stretched, polyamide-based film tube comprising at least one layer and being able to shrink perforated by means of laser light, especially a plastic gut which can be used as an artificial sausage skin



Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2352182 A1 2000/06/08

(21) 2 352 182

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 1999/11/17
(87) Date publication PCT/PCT Publication Date: 2000/06/08
(85) Entrée phase nationale/National Entry: 2001/05/24
(86) N° demande PCT/PCT Application No : EP 99/08824
(87) N° publication PCT/PCT Publication No.: WO 00/32050
(30) Priorité/Priority: 1998/11/27 (198 54 769 2) DE

(51) Cl Int.⁷/Int.Cl.⁷ A22C 13/00
(71) Demandeur/Applicant:
WOLFF WALSRÖDE AG. DE
(72) Inventeurs/Inventors:
KRALLMANN, ANTON, DE;
POPHUSEN, DIRK, DE
(74) Agent: FETHERSTONHAUGH & CO

(54) Titre : BOYAU EN MATIERE PLASTIQUE PERFORE PAR LASER
(54) Title: PLASTIC GUT PERFORATED BY A LASER

(57) Abrégé/Abstract:

The present invention relates to a biaxially stretched, polyamide-based film tube comprising at least one layer and being able to shrink perforated by means of laser light, especially a plastic gut which can be used as an artificial sausage skin

Canada

<http://opic.gc.ca> - Ottawa-Hull K1A 0C9 - <http://cipo.gc.ca>

OPIC · CIPQ 191

OPIC



CIPQ

WW 5521-Foreign Countries

- 15 -

Laser-pinholed plastic skin

Abstract

The present invention relates to a single-layer or multilayer, biaxially drawn, shrinkable, polyamide-based tubular film that is pinholed by means of laser light, in particular to a plastic skin that is capable of being used as a synthetic sausage casing.

Laser-pinholed plastic skin

5 The present invention relates to a single-layer or multilayer, biaxially drawn, shrinkable, polyamide-based tubular film that is pinholed by means of laser light, in particular to a plastic skin that is capable of being used as a synthetic sausage casing.

10 Development in the field of synthetic sausage casings is characterised by the endeavour to make products available that comply with the changed requirements of the meat-processing industry with regard to economy and ecology.

In connection with the industrial production of stewing-sausage and boiling-sausage, biaxially drawn plastic skin based on polyvinylidene-chloride copolymers (PVDC) and polyamide (PA) has proved its worth for many years in a variety of respects. 15 Whereas the market circulation of polyamide-based skin is continuing to rise, in the case of halogen-containing PVDC skin rather a diminishing tendency is to be observed. The very good barrier properties of the PVDC skin cannot offset the known disadvantages, such as high material costs, low thermal stability in the course of thermoplastic processing, low tear-propagation resistance and, not least, its 20 diminishing acceptance by reason of ecological misgivings.

25 In the case of polyamide-based skin, a trend towards multilayer co-extruded skin is emerging which offers advantages in comparison with single-layer products, particularly with regard to the achievable barrier values against water vapour, oxygen and light.

Pure single-layer polyamide skin has been improved by the permeation of water vapour, for example, being reduced through the addition of screening components. In DE 28 50 181 such a single-layer, biaxially stretched casing is described 30 consisting of a polymer mixture formed from aliphatic polyamide and an olefinic copolymer.

5 A five-layer, biaxially stretched tubular film for packaging and wrapping foodstuffs is described in DE 43 39 337. This casing is characterised in that it is synthesised from an inner and an outer layer made of the same polyamide material and from a central polyolefin layer, as well as two adhesion-promoter layers consisting of the same material.

10 A five-layer co-extruded, biaxially drawn tubular film with at least 3 PA layers is described in EP 530 538, wherein polymer layers with a water-vapour-blocking and oxygen-blocking character are included between the inner and outer PA layers

The developments hitherto were consequently pursued mainly in order to make available a shrinkable, high-strength skin with very good barrier values.

15 With some types of sausage meat, however, a certain permeability of the skin is actually required. For this reason, undrawn skins made of plastic are processed further after manufacture by the skin being deliberately provided with small holes. If the diameters of the holes are relatively small and the holes are numerous, these skins are no longer designated as punctured but as pinholed, pricked or perforated synthetic
20 skins.

The state of the art for the pinholing of synthetic skin is presented comprehensively in the book "Wursthüllen Kunstdarm" by G. Effenberger (2nd Edn., Bad Wörishofen 1991, pages 60-62). According to this book, the synthetic skins are pinholed
25 mechanically by needle rollers, but thermal and electrical processes are also known. In the case of mechanical pinholing, the synthetic skin is guided through a pair of rollers. One roller consists of a needle cylinder, which may also be equipped so as to be heatable, whereas the second cylinder, the counterpressure roller, is mostly finished with a rubber, cotton-fleece or felt surface. For the applications that have
30 been described it is sufficient, as a rule, if the needle spacing amounts to about 10 mm and the needle or the hole in the synthetic skin has a diameter of 0.5 to 1 mm.

However, care has to be taken in this case to ensure that pinholing is not effected right into the horizontal edge of the laid-flat synthetic skin, since the reduction in strength arising as a result of the pinholing would otherwise be noticeable there. This is avoided by use being made, for each calibre to be pinholed, of a needle roller
5 of appropriate width and by leaving a sufficient spacing in relation to the horizontal edge. In the course of pinholing it is assumed, as a rule, that 1 to a maximum of 2 holes are present per square centimetre of synthetic-skin surface. But synthetic skins are also known which exhibit a substantially denser holed pattern.

10 A special embodiment of this process for pinholing plastic skin in accordance with the state of the art is described in EP-A 0 845 336.

According to the state of the art as described here, pinholing of drawn plastic skin is not possible, since by reason of the tear-propagation behaviour of drawn polyamide
15 skins the necessary filling-pressure strength is not sufficient.

The object was therefore to make available a tubular film that is capable of being used as plastic skin and that, on the one hand, displays - in addition to the other important requirements resulting from the sausage-production process - a high
20 degree of strength and a good shrinking capacity but, on the other hand, exhibits a local permeability making it possible, on the one hand, for gases such as arise, for example, in the course of the ripening of spreading-sausage consisting of onion and spiced mincemeat (Zwiebelmettwurst) to escape from the casing but, on the other hand, also for gases and liquids to reach the contents through the casing from outside,
25 for example in order to smoke the contents or to guarantee a ripening process in the case of raw sausage.

This object was achieved through the provision of a tubular film, in particular of a plastic skin, that is biaxially drawn, single-layered or multilayered, shrinkable and
30 polyamide-based and that has been pinholed by means of laser light. The term polyamide-based here is to be understood to mean that at least one layer of the

tubular film consists predominantly - i.e., in a proportion amounting to at least 50 %
- of polyamide, optionally also in the form of a copolymer or a blend.

5 The film may be extruded directly so as to form a tubular film or may firstly be
produced in the form of a flat film and heat-sealed at a later time so as to form a tube.

10 Surprisingly, it has been shown in the tests which have been carried out and in the
practical-application experiments with samples produced in accordance with the
invention that no reduction in the strength of the tubular film occurs as a result of the
bombardment with laser light and that tears emanating from the holes, such as are
known in the case of punching with needles, do not arise. Furthermore, it is also
possible for smaller hole diameters to be produced than can be attained with
traditional needle pinholing.

15 The use of lasers in the field of the production and processing of synthetic skin was
mainly restricted hitherto to altering the surface characteristics, such as surface
polarities, and to the measurement of geometric magnitudes.

20 Production of such synthetic skins according to the invention can be effected by a
single-layer or multilayer, biaxially drawn, shrinkable, polyamide-based tubular film
which has been produced by conventional processes being irradiated by means of
laser light. Preferably, a biaxially oriented tubular film which has been produced in
the double-bubble process is irradiated with laser light.

25 The conventional double-bubble process can be subdivided into the following
process steps:

1. Extrusion, calibration and cooling of the primary tube to be drawn
2. Reheating of the primary tube to a suitable drawing temperature

3. Biaxial stretching by applying a pressure difference between the inner volume of the tube and the environment of the tube as well as by the longitudinal draw-off force assisting the longitudinal stretching
4. Thermosetting of the biaxially drawn tubular film
5. Winding-up and subsequent offline processing steps (gathering etc)

The term biaxial stretching is understood by a person skilled in the art to mean the transverse and longitudinal stretching of the thermoplastic extrudate at temperatures between glass transition temperature and melting-temperature of the polymeric materials. Biaxial drawing is conventionally effected by means of a bubble which is filled with a pressure cushion of gas or fluid and which is included in gas-tight or fluid-tight manner between two pairs of rollers running at differing peripheral speeds. Whereas the ratio of the differing peripheral speeds of the rollers corresponds to the degree of longitudinal stretching, the degree of transverse stretching is calculated from the ratio of the diameter of the tube in the drawn state to that of the undrawn primary tube. The draw ratio (DR) reflects the quotient derived from the degree of transverse stretching and the degree of longitudinal stretching, the degree of surface draw (SD) results from the product of the degree of longitudinal stretching and the degree of transverse stretching.

The biaxially stretched tubular film according to the invention is produced in a diameter range (calibre range) between 30 and 150 mm, which is typical of stewing-sausage and boiling-sausage applications. The thickness of the co-extruded film ranges in preferred embodiments between 35 and 70 micrometers.

During the stretching, the molecules of the tubular film which is in the solid state are aligned in such a manner that the modulus of elasticity and the strength values in both the transverse and longitudinal directions are increased to a considerable degree. As a result of the stretching and subsequent temperature treatment (thermosetting), the shrinkage of the film is adjusted at the same time.

Sufficient strength obtains when the packaging casing is mainly deformed elastically in the course of the filling operation and during the pasteurisation or sterilisation. At the same time, the packaging casing has to retain its cylindrical shape and must not bulge or bend.

5

Treatment with laser light of the tubular film which has been produced in this way may be effected inline, immediately subsequent to thermosetting, or as a separate, subsequent processing step.

10 CO₂ lasers have proved particularly suitable for the processing of polyamide skin, since they operate in a wavelength range in which polyamide exhibits suitable transmission. For the processing of plastics, Nd:YAG lasers and excimer lasers have also proved their worth for cutting tasks. In principle, these may likewise be employed for production of the tubular film according to the invention, but by reason
15 of the transmission properties of polyamide they are less suitable. As a rule, the unfocused laser beam of the laser-light source is concentrated by means of a focusing lens. After adjustment of the preferably laid-flat tubular film in the focal plane, the focal point of the laser, the perforation can be carried out, depending on the adjusted intensity and on the draw-off speed and feed speed of the tubular film, for the
20 purpose of achieving the desired diameters of the holes. It is possible for multiple perforation to be obtained with only one source of laser light, for example by moving the light source at right angles to the draw-off direction of the tubular film or by using a perforated plate. Perforation may be effected separately on the upper side and underside of the skin, either by use being made of several sources of laser light
25 or by the laser light being routed via appropriate beam-splitters and mirrors. The obtainable bore diameter generally amounts, depending on the process parameters that have been set, to between 10 and 1,000 µm, in particular between 100 and 300 µm. The intensity of the lasers should be selected in a manner depending on the chosen arrangement of the lasers and the number of perforations to be undertaken
30 simultaneously. The installed power conventionally lies in the range between 2 and 2,000 W, in particular between 20 and 200 W.

WW 5521-Foreign Countries

- 7 -

The following Examples and Comparative Examples are intended to clarify the invention.

Tests:

Ascertainment of the pressure-expansion behaviour with measurement of the bursting pressure and bursting calibre.

5

In this connection a skin which is sealed on one side is pressurised on the inside, for example with the aid of a water column, and the diameter (calibre) arising with increasing pressure is recorded metrologically. The maximum pressure and the calibre arising in the process until the casing tears away or bursts are recorded as bursting pressure and bursting calibre.

10

Practical-application filling experiments with appraisal of the marketability of the filling machine, measurement of the filling calibre and finished calibre and appraisal of the appearance of the sample sausages produced. The appraisal is undertaken by awarding marks.

15

Measurement of the hole pattern (mean hole diameter, hole spacing) by means of microscopic measurement.

Examples:

The various polymers employed in tubular films according to the invention and in the Comparative Examples are abbreviated as follows:

5

PA	polyamide 6	e.g.: Durethan B40 F (Bayer AG)
PO-HV	propylene-based copolymer adhesion promoter	e.g.: Bynel E 379 (DuPont)
XX	ethylene/vinyl-alcohol copolymer	e.g.: EVAL LC F 101 BZ (Kuraray)
APA	partially aromatic copolyamide	e.g.: Selar PA 3426 (DuPont)
MB	master batch based on polyamide 6	e.g.: colour master batch PA gold

Example 1 (E1):

The commercial product Walsroder® K plus SK, a five-layer, drawn, polyamide-based plastic skin with rated calibre 60 mm (manufacturer Wolff Walsrode AG, Walsrode), laid flat, is conducted stepwise past the laser source, which is mobile at right angles to the feed direction of the tubular film, and is perforated by means of a Synrad CO₂ laser. The hole spacing in and parallel to the feed direction amounts to 10 mm, and the individual hole diameter amounts on average to 150 µm. The CO₂ laser operates at a wavelength of $\lambda = 10.6 \mu\text{m}$ and at a mean power of $P = 50 \text{ W}$.

Comparative Example 1.1 (CE1.1):

The skin which was used in Example 1 is not pinholed.

20

Comparative Example 1.2 (CE1.2):

The skin which was used in Example 1 is pinholed mechanically by means of needles, so that the hole spacing in and parallel to the feed direction amounts to 10 mm and the individual hole diameter amounts on average to 500 µm.

25

Example 2 (E2):

The commercial product Walsroder® K flex rot, a five-layer, drawn, polyamide-based plastic skin with rated calibre 45 (manufacturer Wolff Walsrode AG, Walsrode), laid flat, is conducted stepwise past the laser source, which is mobile at right angles to the feed direction of the tubular film, and is perforated by means of a Synrad CO₂ laser. The hole spacing in and parallel to the feed direction amounts to 10 mm, and the individual hole diameter amounts on average to 150 µm. The CO₂ laser operates at a wavelength of $\lambda = 10.6 \mu\text{m}$ and at a mean power of $P = 50 \text{ W}$.

Comparative Example 2 (CE2):

The skin which was used in Example 2 is pinholed mechanically by means of needles, so that the hole spacing in and parallel to the feed direction amounts to 10 mm and the individual hole diameter amounts on average to 500 µm.

Example 3 (E3):

A three-layer plastic skin was produced with the aid of the double-bubble process. Via a multilayer nozzle a primary tube was extruded which was subsequently biaxially stretched simultaneously at a surface temperature of 90 °C.

The skin then has a laid-flat width of 97 mm and a total thickness of 45 µm.

25 The layer structure is: (inside) PA / PO-HV / PA (outside)
Thickness profile: (inside) 10 / 10 / 25 (outside)

As described in Examples 1 and 2, the skin is conducted through a laser unit and perforated by means of a CO₂ laser. The hole spacing in and parallel to the feed direction amounts to 10 mm, and the individual hole diameter amounts on average to

150 μm . The CO_2 laser operates at a wavelength of $\lambda = 10.6 \mu\text{m}$ and at a mean power of $P = 60 \text{ W}$.

Example 4 (E4):

5

A five-layer plastic skin was produced with the aid of the double-bubble process. Via a multilayer nozzle a primary tube was extruded which was subsequently biaxially stretched simultaneously at a surface temperature of 90°C .

10

The skin then has a laid-flat width of 97 mm and a total thickness of 55 μm .

The layer structure is: (inside) PA / PA + MB + aPA / PO-HV / PA + MB + aPA / PA (outside)

Thickness profile: (inside) 5 / 20 / 5 / 20 / 5 (outside)

15

The skin is conducted through a laser unit and perforated by means of a CO_2 laser. The hole spacing in and parallel to the feed direction amounts to 10 mm, and the individual hole diameter amounts on average to 150 μm . The CO_2 laser operates at a wavelength of $\lambda = 10.6 \mu\text{m}$ and at a mean power of $P = 60 \text{ W}$.

20

Example 5 (E5):

A five-layer plastic skin was produced with the aid of the double-bubble process. Via a multilayer nozzle a primary tube was extruded which was subsequently

25

The skin then has a laid-flat width of 97 mm and a total thickness of 40 μm .

The layer structure is: (inside) PA / PO-HV / XX / PA + MB + aPA / PA (outside)

30

Thickness profile: (inside) 5 / 5 / 5 / 20 / 5 (outside)

- 12 -

As described in Examples 1 and 2, the skin is conducted through a laser unit and perforated by means of a CO₂ laser. The hole spacing in and parallel to the feed direction amounts to 10 mm, and the individual hole diameter amounts on average to 150 µm. The CO₂ laser operates at a wavelength of $\lambda = 10.6 \mu\text{m}$ and at a mean
5 power of $P = 60 \text{ W}$.

The samples from the Examples and Comparative Examples were subsequently gathered up and, on the basis of pressure-expansion curves, examined for their mechanical strength and, in the practical-application filling experiment with
10 Zwiebelmettwurst, for their suitability in practice. The results of the tests are compiled in the following Table:

WW 5521-Foreign Countries

- 13 -

Sample		E1	CE1.1	CE1.2	E2	CE2	E3	E4	E5
Horizontal width	mm	97	97	97	67	67	97	97	97
Test calibre at 10 kPa	mm	61.9	61.9	61.9	42.1	42.7	62	61.8	62.5
Test calibre at 20 kPa	mm	62.6	62.5	burst	42.9	burst	63	62.3	63.5
Test calibre at 40 kPa	mm	65.8	65.9	-	45.8	-	65	64	66.5
Test calibre at 60 kPa	mm	69	69.5	-	50.2	-	67.5	66	71
Bursting pressure	kPa	65	67	18	81	15	90	80	>100
Bursting calibre	mm	70.1	70.6	62.3	64.7	43	70	68	73
Filling behaviour	mark	1	1	6 (cracks)	1	5 (cracks)	1	2	1
Achievable filling calibre	mm	63-64	63-64	61	43-44	42	64	64	64-65
Loss of sausage meat during filling (Zwiebel-metzwurst)		slight	none	con- siderable	slight	con- siderable	slight	slight	slight
Optics (Zwiebel-metzwurst)	mark	1	3 (gas bubbles)	3-4 (wrinkles)	1	3-4 (wrinkles)	3	2	1

Claims

1. Single-layer or multilayer, biaxially drawn, shrinkable, polyamide-based tubular film which is pinholed by means of laser light.
- 5 2. Tubular film according to claim 1, wherein the hole diameter of the individual pinholed holes amounts to between 10 and 1,000 μm , in particular between 100 and 300 μm .
- 10 3. Tubular film according to claim 1 or 2, wherein the laser light which is used for pinholing is generated by a CO_2 laser.
4. Tubular film according to one of claims 1 to 3 with a total thickness from 30 to 70 μm .
- 15 5. Use of a tubular film according to one of claims 1 to 4 as plastic skin in the production of sausages.
- 20 6. Process for the production of a tubular film according to one of claims 1 to 4, wherein a biaxially oriented, polyamide-based tubular film which is produced in accordance with the double-bubble process is conducted in a separate processing step or preferably inline past at least one focused CO_2 laser and in the process is treated with laser light of an intensity sufficient to pinhole the tubular film.
- 25 7. Process according to claim 6, wherein the tubular film, laid flat, is conducted past at least one focused CO_2 laser.